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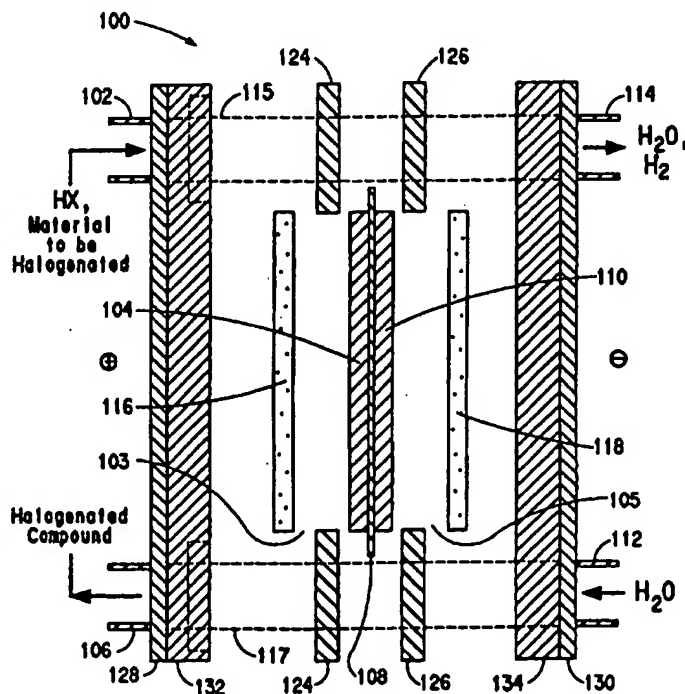
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(54) Title: IN-SITU HALOGENATION OF COMPOUNDS IN AN ELECTROCHEMICAL CELL

(57) Abstract

The present invention relates to an electrochemical cell and a process for in-situ halogenation of compounds. In this process, anhydrous hydrogen halide is supplied to an anode-side inlet (102) of an electrochemical cell (100), and a material to be halogenated is co-fed to the cell. The hydrogen halide is oxidized at the anode (104) of the cell to produce a halogenating species. The halogenating species reacts with the co-fed material to produce a halogenated compound.



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TITLEIN-SITU HALOGENATION OF COMPOUNDS  
IN AN ELECTROCHEMICAL CELL**BACKGROUND OF THE INVENTION**5 1. Field of the Invention

The present invention relates to a process and an electrochemical cell for halogenating compounds.

2. Description of the Related Art

10 Using an electrolytically activated fluoride ion produced by an electrochemical cell as its primary means of fluorination is a known direct fluorination method. In this method, invented by Simons, (see, e.g., U.S. Patent No. 2,490,099) organic precursors are dissolved in liquid hydrogen fluoride and a  
15 voltage slightly under the voltage required for generation of elemental fluorine is applied across carbon electrodes. This technique is practiced widely by Minnesota Mining & Manufacturing Co. (3M) of St. Paul, Minnesota. This technique has been a  
20 successful source of organofluorine compounds, functional fluids and low molecular weight perfluoro-carbon acids and diacids. There are also a number of companies in Japan and Europe that use electrochemical fluorination for production of fluorocarbons. See,  
25 *Kirk-Othmer, Encyclopedia of Chemical Technology, Fourth Ed., Volume 11, John Wiley & Sons (1994), pp. 484-485.*

Electrochemical fluorination as developed by Simons utilizes liquid hydrogen fluoride as a reactant  
30 and solvent. The principal disadvantage to this technique is the requirement that the organic material be at least somewhat soluble in the polar liquid hydrogen fluoride. Liquid or solid starting materials may be dissolved or suspended in the liquid hydrogen  
35 fluoride. Also, gaseous starting materials may be bubbled into the liquid.

Therefore, there exists a need for a process for electrochemical fluorination of organic compounds

which does not employ liquid hydrogen fluoride as a reaction media.

#### SUMMARY OF THE INVENTION

The present invention solves the problems of the prior art by providing an electrochemical cell and a process which does not employ liquid hydrogen fluoride as a reaction media, and hence does not suffer from the disadvantage of requiring solubility in liquid hydrogen fluoride. The fact that the process of the present invention operates in the absence of any solvent or reaction media removes a potential source of by-products and/or impurities during product isolation.

Therefore, in accordance with the present invention, there is provided a process and an electrochemical cell and for the in-situ production of a halogenated compound from anhydrous hydrogen halide. In this process, anhydrous hydrogen halide and a material to be halogenated are co-fed to an electrochemical cell. The electrochemical cell comprises an anode and a cathode, and a membrane having one side disposed in contact with the anode and another side disposed in contact with the cathode. A voltage is applied to the cell so that the anode is at a higher potential than the cathode. The hydrogen halide is oxidized at the anode to produce a halogenating species, which reacts with the co-fed material to produce a halogenated compound. The halogenated compound is released from the cell, along with any unreacted hydrogen halide and co-fed material.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic diagram showing the details of an electrochemical cell for producing halogen gas from anhydrous hydrogen halide according to the present invention.

Fig. 1A is a cut-away, top cross-sectional view of the anode and cathode mass flow fields as shown in Fig. 1.

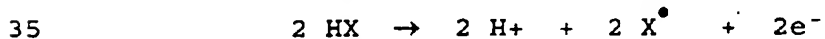
### DESCRIPTION OF THE PREFERRED EMBODIMENTS

Reference will now be made in detail to the present preferred embodiments of the invention as illustrated in the accompanying drawings.

5 In accordance with the present invention, there is provided an electrochemical cell for producing in-situ a halogenated compound. Such a cell is shown at 100 in Fig. 1. The electrochemical cell of the present invention comprises inlet means for supplying  
10 anhydrous hydrogen halide to the cell. The inlet means comprises an anode-side inlet 102 as shown in Fig. 1 which supplies anhydrous hydrogen halide (i.e., in vapor or molecular form) to the cell. The inlet means is also for co-feeding a material to be  
15 halogenated to the cell. This material is co-fed also in vapor form to the anode-side inlet of the cell.

The electrochemical cell of the present invention comprises means for oxidizing the hydrogen halide to produce protons and a halogenating species. More  
20 particularly, the oxidizing means oxidizes anhydrous hydrogen halide (i.e., in vapor or molecular form). The oxidizing means comprises an electrode, or more specifically, an anode 104 as shown in Fig. 1. The electrochemical cell of the present invention also  
25 comprises an anode chamber disposed adjacent the oxidizing means. An anode chamber is shown at 103 in Figs. 1 and 1A disposed adjacent, meaning next to or near, the oxidizing means, or anode.

The reaction at the anode-side of the cell of the present invention is the oxidation of hydrogen halide to produce protons and a halogenating species  
30 according to the following generic equation, where HX is a hydrogen halide, and  $X^\bullet$  is a halogenating species.



The material to be halogenated, i. e., the starting material to be fed to the anode side of the cell of the present invention, or the co-fed material,

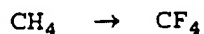
is a chemical compound capable of reacting with a halogenating species generated. According to the present invention, the co-fed material is reacted with the halogenating species in the cell to produce a  
5 halogenated compound.

The material to be halogenated may be of the class of organic compounds that possesses a hydrogen atom capable of being replaced by the halogenating species, i.e.,  
10



where X is a halogen.

Conversions of this type include the conversion  
15 of methane to tetrafluoromethane and trifluoromethane to tetrafluoromethane, the hydrogen halide being hydrogen fluoride.



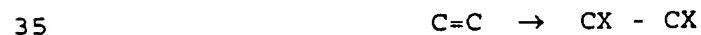
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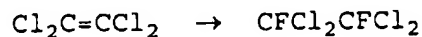
A further example is the conversion of methane to carbon tetrachloride, the hydrogen halide being  
25 hydrogen chloride.



The material to be halogenated may be of the  
30 class of organic compounds that possesses a carbon-carbon double bond capable of adding the halogenating species to both carbon atoms of the carbon-carbon double bond., i.e.

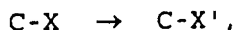


Conversions of this type include the conversion of perchloro ethylene to tetrachloro difluoro ethane, the hydrogen halide being hydrogen fluoride  
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The material to be halogenated may also be of the class of organic compounds that possesses a halogen atom capable of being replaced by the (different) halogenating species, i.e.

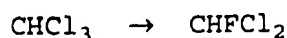
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where X and X' are different halogens.

Conversions of this type include the conversion of chloroform to chlorodifluoromethane, the hydrogen halide being hydrogen fluoride.

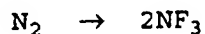
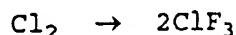
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The compound to be halogenated may also be inorganic. These conversions are exemplified by the conversions of chlorine to chlorine trifluoride and nitrogen to nitrogen trifluoride by reaction with hydrogen fluoride.

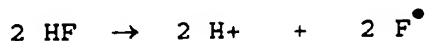
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While not wishing to be bound by any mechanism, it is believed that in most, if not all, conversions the halogenating species is the halogen radical which is generated at the anode, as illustrated below for the fluorine radical.

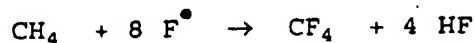
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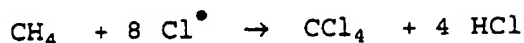
The chemical conversions described above are, thus, posed to be the product of starting material with the halogen radical.

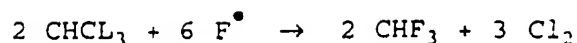
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For example:



40





5        The reaction at the cathode-side of the cell of  
the present invention consists of the reduction of  
protons according to one or both of the following  
equations.



The electrochemical cell of the present invention also outlet means for releasing the halogenated compound. The outlet means comprises an anode-side outlet 106 as shown in Fig. 1. A portion of the anhydrous hydrogen halide and a portion of the co-fed material may be unreacted, and these unreacted portions leave the electrochemical cell through the anode-side outlet, along with the halogenated compound.

The electrochemical cell of the present invention also comprises cation-transporting means for transporting the protons therethrough, wherein the oxidizing means is disposed in contact with one side of the cation-transporting means. Preferably, the cation-transporting means is a cation-transporting membrane 108, where the anode is disposed in contact with one side of the membrane as shown in Figs. 1 and 1A. More specifically, membrane 108 may be a proton-conducting membrane. In the present invention, the membrane acts as the electrolyte. The membrane may be a commercial cationic membrane made of a fluoro- or perfluoropolymer, preferably a copolymer of two or more fluoro or perfluoromonomers, at least one of which has pendant sulfonic acid groups. The presence of carboxylic groups is not desirable, because those groups tend to decrease the conductivity of the membrane when they are protonated. Various suitable resin materials are available commercially or can be made according to the patent literature. They include

fluorinated polymers with side chains of the type  
—CF<sub>2</sub>CFRSO<sub>3</sub>H and —OCF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>SO<sub>3</sub>H, where R is an F, Cl,  
CF<sub>2</sub>Cl, or a C<sub>1</sub> to C<sub>10</sub> perfluoroalkyl radical. The  
membrane resin may be, for example, a copolymer of  
5 tetrafluoroethylene with CF<sub>2</sub>=CFOCF<sub>2</sub>CF(CF<sub>3</sub>)OCF<sub>2</sub>CF<sub>2</sub>SO<sub>3</sub>H.  
Sometimes those resins may be in the form that has  
pendant —SO<sub>2</sub>F groups, rather than —SO<sub>3</sub>H groups. The  
sulfonyl fluoride groups can be hydrolyzed with  
potassium hydroxide to —SO<sub>3</sub>K groups, which then are  
10 exchanged with an acid to —SO<sub>3</sub>H groups. Suitable  
perfluorinated cationic membranes, which are made of  
hydrated copolymers of polytetrafluoroethylene and  
poly-sulfonyl fluoride vinyl ether-containing pendant  
sulfonic acid groups, are offered DuPont under the  
15 trademark "NAFION®" (hereinafter referred to as  
NAFION®). In particular, NAFION® membranes containing  
pendant sulfonic acid groups include NAFION® 115,  
NAFION® 117, NAFION® 324 and NAFION® 417. The first  
and second types of NAFION® are unsupported and have an  
20 equivalent weight of 1100 g., equivalent weight being  
defined as the amount of resin required to neutralize  
one liter of a 1M sodium hydroxide solution.  
NAFION® 324 and NAFION® 417 are both supported on a  
fluorocarbon fabric, the equivalent weight of  
25 NAFION® 417 also being 1100 g. NAFION® 324 has a two-  
layer structure, a 125 µm-thick membrane having an  
equivalent weight of 1100 g., and a 25 µm-thick  
membrane having an equivalent weight of 1500 g.  
NAFION® 115 in particular may be used with the  
30 electrochemical cell of the present invention.

Although the present invention describes the use  
of a solid polymer electrolyte membrane, it is well  
within the scope of the invention to use other cation-  
transporting membranes which are not polymeric. For  
35 example, proton-conducting ceramics such as beta-  
alumina may be used. Beta-alumina is a class of  
nonstoichiometric crystalline compounds having the  
general structure Na<sub>2</sub>O<sub>x</sub>·Al<sub>2</sub>O<sub>3</sub>, in which x ranges from 5

00( $\beta$ "-alumina) to 11 ( $\beta$ -alumina). This material and a number of solid electrolytes which are useful for the invention are described in the Fuel Cell Handbook, A. J. Appleby and F. R. Foulkes, Van Nostrand Reinhold, N.Y., 1989, pages 308-312. Additional useful solid state proton conductors, especially the cerates of strontium and barium, such as strontium ytterbiate cerate ( $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$ ) and barium neodymate cerate ( $\text{BaCe}_{0.9}\text{Nd}_{0.01}\text{O}_{3-\alpha}$ ) are described in a final report, DOE/MC/24218-2957, Jewulski, Osif and Remick, prepared for the U.S. Department of Energy, Office of Fossil Energy, Morgantown Energy Technology Center by Institute of Gas Technology, Chicago, Illinois, December, 1990.

The electrochemical cell of the present invention also comprises means for reducing the transported protons, where the reducing means is disposed in contact with the other side of the cation-transporting means. The reducing means comprises an electrode, or more specifically, a cathode 110, where cathode 110 is disposed in contact with the other side (as opposed to the side which is in contact with the anode) of membrane 108 as illustrated in Figs. 1 and 1A.

The electrochemical cell of the present invention also includes a cathode chamber disposed adjacent the reducing means. A cathode chamber is shown at 105 in Figs. 1 and 1A disposed adjacent to, meaning next to or near, the reducing means, or cathode. The electrochemical cell of the present invention also comprises cathode-side inlet means for supplying water to the membrane. The cathode-side inlet means comprises a cathode-side inlet 112 as shown in Fig. 1. The cathode-side inlet is disposed in fluid communication with the cathode chamber. The electrochemical cell of the present invention also comprises cathode-side outlet means also disposed in fluid communication with the cathode chamber. The cathode-side outlet means comprises a cathode-side outlet 114 as shown in

Fig. 1. A passage 115 as shown in Fig. 1 is formed between the anode-side inlet and the cathode-side outlet, and a similar passage 117 is shown formed between the cathode-side inlet and the anode-side outlet. These passages carry the reactants into and the products out of the cell through the anode and cathode-side inlets, and the anode and cathode-side outlets, as will be further explained below.

The anode and the cathode comprise an electrochemically active material. The electrochemically active material may comprise any type of catalytic or metallic material or metallic oxide, as long as the material can support charge transfer. Preferably, the electrochemically active material may comprise a catalyst material such as platinum, ruthenium, osmium, rhenium, rhodium, iridium, palladium, gold, titanium, tin or zirconium and the oxides, alloys or mixtures thereof. Other catalyst materials suitable for use with the present invention may include, but are not limited to, transition metal macro cycles in monomeric and polymeric forms and transition metal oxides, including perovskites and pyrochores.

The anode and the cathode may be porous, gas-diffusion electrodes. Gas diffusion electrodes provide the advantage of high specific surface area, as known to one skilled in the art. A particular type of gas diffusion electrode, known as an ELAT, may be used as the anode and the cathode. An ELAT comprises a support structure, as well as the electrochemically active material. In one preferred embodiment, an ELAT comprising a support structure of carbon cloth and electrochemically active material comprising ruthenium oxide, commercially available from E-TEK, of Natick, Massachusetts, may be used. Alternatively, an ELAT may be used which comprises a catalyst material mixed with carbon and particles of polytetrafluoroethylene, or PTFE, a tetrafluoropolymer resin which is sold under the trademark "TEFLON®" (hereinafter referred to

as "PTFE"), commercially available from DuPont. The catalyst material, carbon particles and PTFE are then sintered on a carbon cloth substrate, which is treated with a NAFION<sup>®</sup> solution. This ELAT is held  
5 mechanically against the membrane of the cell.

Alternative arrangements of the electrochemically active material may be used for the anode and cathode of the present invention. The electrochemically active material may be disposed adjacent, meaning at  
10 or under, the surface of the cation-transporting membrane. For instance, the electrochemically active material may be deposited into the membrane, as shown in U.S. Patent No. 4,959,132 to Fedkiw. A thin film of the electrochemically active material may be  
15 applied directly to the membrane. Alternatively, the electrochemically active material may be hot-pressed to the membrane, as shown in A. J. Appleby and E. B. Yeager, Energy, Vol. 11, 137 (1986).

If the electrodes are hot-pressed into the  
20 membrane, they have the advantage of having good contact between the catalyst and the membrane. In a hot-pressed electrode, the electrochemically active material may comprise a catalyst material on a support material. The support material may comprise particles  
25 of carbon and particles of PTFE. The electrochemically active material may be bonded by virtue of the PTFE to a support structure of carbon cloth or paper or graphite paper and hot-pressed to the cation-transporting membrane. The hydrophobic nature of PTFE  
30 does not allow a film of water to form at the anode. A water barrier in the electrode would hamper the diffusion of HCl to the reaction sites.

The loadings of electrochemically active material may vary based on the method of application to the  
35 membrane. Hot-pressed, gas-diffusion electrodes typically have loadings of 0.10 to 0.50 mg/cm<sup>2</sup>. Lower loadings are possible with other available methods of deposition, such as distributing them as thin films

from inks onto the membranes, to form a catalyst-coated membrane, as described in Wilson and Gottesfeld, "High Performance Catalyzed Membranes of Ultra-low Pt Loadings for Polymer Electrolyte Fuel Cells", Los Alamos National Laboratory, J. Electrochem. Soc., Vol. 139, No. 2 L28-30, 1992, where the inks contain solubilized NAFION® to enhance the catalyst-ionomer surface contact and to act as a binder to the NAFION® perfluorinated membrane sheet. With such a system, loadings as low as 0.017 mg active material per cm<sup>2</sup> have been achieved.

In one embodiment, a thin film of the electrochemically active material is be applied directly to the membrane to form a catalyst-coated membrane. In this preferred embodiment, the membrane is typically formed from a polymer as described above in its sulfonyl fluoride form, since it is thermoplastic in this form, and conventional techniques for making films from thermoplastic polymer can be used. The electrochemically active material is conventionally incorporated in a coating formulation, or "ink", which is applied to the membrane. The coating formulation, and consequently the anode and the cathode after the catalyst coated membrane is formed, also comprises a binder polymer for binding the particles of the electrochemically active material together. When the binder polymer is in the sulfonyl fluoride form, the solvent can be a variety of solvents, such as FLUORINERT FC-40, commercially available from 3M of St. Paul, Minnesota, which is a mixture of perfluoro(methyl-di-n-butyl)amine and perfluoro(tri-n-butylamine). In this embodiment, a copolymer polymerized from tetrafluoroethylene and a vinyl ether which is represented by the formula  $\text{CF}_2=\text{CF}-\text{O}-\text{CF}_2\text{CF}(\text{CF}_3)-\text{O}-\text{CF}_2\text{CF}_2\text{SO}_2\text{F}$  has been found to be a suitable binder polymer. In addition, ruthenium dioxide has been found to be a suitable catalyst. The sulfonyl fluoride form has been found to be compatible

with FC-40 and to give a uniform coating of the ruthenium dioxide catalyst on the membrane.

If a catalyst-coated membrane as described above is used, the electrochemical cell must include a gas diffusion layer (not shown) disposed in contact with the anode and the cathode, respectively, (or at least in contact with the anode), on the side of the anode or cathode opposite the side which is in contact with the membrane. The gas diffusion layer provides a porous structure that allows the anhydrous hydrogen chloride to diffuse through to the layer of electrochemically active material of the catalyst-coated membrane. In addition, both the anode gas diffusion layer and the cathode gas diffusion layer distribute current over the electrochemically active material, or area, of the catalyst-coated membrane. The diffusion layers are preferably made of graphite paper, and are typically 15 - 20 mil thick.

When using any type of membrane and electrodes with the present invention, the membrane must be kept hydrated in order to increase the efficiency of proton transport through the membrane. This keeps the conductivity of the membrane high. In the present invention, the hydration of the membrane is obtained by keeping liquid water in contact with the cathode-side of the membrane. For example, when using gas diffusion electrodes, liquid water is delivered to the cathode, and the liquid water passes through the gas-diffusion electrode and contacts the membrane. When using a catalyst-coated membrane, liquid water is delivered to the membrane itself, since the cathode is a thin layer of electrochemically active material applied directly to the membrane.

In particular, in the first embodiment, water is added to the electrochemical cell through cathode-side inlet 112. The protons which are produced by the oxidation of the hydrogen halide are transported through the membrane and reduced at the cathode to

form hydrogen gas. This hydrogen gas is evolved at the interface between the cathode and the membrane. The hydrogen gas, which is shown as  $H_2$  in Fig. 1, exits the cell through the cathode-side outlet. In addition, a portion of the water supplied to the cathode-side inlet is released through the cathode-side outlet, as shown as  $H_2O$  in Fig. 1.

Returning again to the description of Fig. 1, the electrochemical cell of the present invention further comprises an anode flow field 116 disposed in contact with the anode and a cathode flow field 118 disposed in contact with the cathode as shown in Figs. 1 and 1A. The flow fields are electrically conductive, and act as both mass and current flow fields. Preferably, the anode and the cathode flow fields comprise porous graphite paper. Such flow fields are commercially available from Spectracorp, of Lawrence, Massachusetts. However, the flow fields may be made of any material and in any manner known to one skilled in the art. For example, the flow fields may alternatively be made of a porous carbon in the form of a foam, cloth or mat. For the purpose of acting as mass flow fields, the anode mass flow field includes a plurality of anode flow channels 120, and the cathode mass flow field includes a plurality of cathode flow channels 122 as shown in Fig. 1A, which is a cut-away, top cross-sectional view showing only the flow fields of Fig. 1. Preferably, the channels of the anode mass flow field and the channels of the cathode mass flow field are parallel to each other, and more particularly, are vertical and parallel to each other. The anode flow fields and the anode flow channels get reactants, i.e., hydrogen halide and the co-fed material, to the anode and products, i.e., the halogenated compound, and any unreacted hydrogen halide and co-fed material, from the anode. The cathode flow field and the cathode flow channels get catholyte, such as liquid water to the membrane and

products, such as hydrogen gas and water, from the cathode.

The electrochemical cell of the present invention may also comprise an anode-side gasket 124 and a cathode-side gasket 126 as shown in Fig. 1. Gaskets 124 and 126 form a seal between the interior and the exterior of the electrochemical cell. Preferably, the anode-side gas is made of a fluoroelastomer, sold under the trademark VITON® (hereinafter referred to as VITON®) by DuPont Dow Elastomers L.L.C. of Wilmington, Delaware. The cathode-side gasket may be made of the terpolymer ethylene/propylene/diene (EPDM), sold under the trademark NORDEL® by DuPont, or it may be made of VITON®.

The electrochemical cell of the present invention also comprises an anode current bus 128 and a cathode current bus 130 as shown in Fig. 1. The current buses conduct current to and from a voltage source (not shown). Specifically, anode current bus 128 is connected to the positive terminal of a voltage source, and cathode current bus 130 is connected to the negative terminal of the voltage source, so that when voltage is applied to the cell, current flows through all of the cell components to the right of current bus 128 as shown in Fig. 1, including current bus 130, from which it returns to the voltage source. The current buses are made of a conductor material, such as copper.

The electrochemical cell of the present invention may further comprise an anode current distributor 132 as shown in Fig. 1. The anode current distributor collects current from the anode current bus and distributes it to the anode by electronic conduction. The anode current distributor may comprise a fluoropolymer which has been loaded with a conductive material. In one embodiment, the anode current distributor may be made from polyvinylidene fluoride, sold under the trademark KYNAR® (hereinafter referred

to as "KYNAR®") by Elf Atochem North America, Inc. Fluoropolymers, and graphite.

The electrochemical cell of the present invention may further comprise a cathode current distributor 134 as shown in Fig. 1. The cathode current distributor collects current from the cathode and for distributing current to the cathode bus by electronic conduction. The cathode distributor also provides a barrier between the cathode current bus and the cathode and the hydrogen halide. Like the anode current distributor, the cathode current distributor may comprise a fluoropolymer, such as KYNAR®, which has been loaded with a conductive material, such as graphite.

The electrochemical cell of the present invention also includes an anode-side stainless steel backer plate (not shown), disposed on the outside of the cell next to the anode current distributor, and a cathode-side stainless steel backer plate (also not shown), disposed on the outside of the cell next to the cathode current distributor. These steel backer plates have bolts extending therethrough to hold the components of the electrochemical cell together and add mechanical stability thereto.

When more than one anode-cathode pair is used, such as in manufacturing, a bipolar arrangement, as familiar to one skilled in the art, is preferred. The electrochemical cell of the present invention may be used in a bipolar stack. To create such a bi-polar stack, anode current distributor 132 and every element to the right of the anode current distributor as shown in Fig. 1, up to and including cathode current distributor 134, are repeated along the length of the cell, and current buses are placed on the outside of the stack.

Further in accordance with the present invention, there is provided a process for the in-situ production of a halogenated compound. In operation, a voltage is

applied to the anode and the cathode so that the anode is at a higher potential than the cathode, and current flows to the anode bus. Anode current distributor 132 collects current from the anode bus and distributes it to the anode by electronic conduction. Anhydrous hydrogen halide is supplied to anode-side inlet 102 and through flow channels 120 in the anode mass flow field 116. The hydrogen halide is transported to the surface of anode 104. Hydrogen halide is oxidized at the anode under the potential created by the voltage source to produce a halogenating species and protons ( $H^+$ ) at the anode. The co-fed material reacts with the halogenating species to produce a halogenated compound. The halogenated compound is released from anode-side outlet 106 of the electrochemical cell as shown in Fig. 1. A portion of the hydrogen halide and a portion of the co-fed material may be unreacted in the cell. In this case, the unreacted hydrogen halide and co-fed material are also released from the anode-side outlet.

The protons are transported through the membrane, which acts as an electrolyte. The transported protons are reduced at the cathode. Water is delivered to the cathode through a cathode-side inlet, such as cathode-side inlet 112 as shown in Fig. 1 and through the channels in the cathode mass flow field, such as channels 122 in cathode mass flow field 118 to hydrate the membrane and thereby increase the efficiency of proton transport through the membrane. In the present invention, the hydrogen which is evolved at the interface between the cathode and the membrane exits via cathode-side outlet 114, along with a portion of the water which is delivered to the cathode-side inlet. The hydrogen bubbles through the water and is not affected by the electrode. Cathode current distributor 134 collects current from cathode 110, and distributes it to cathode bus 130.

In the process of the present invention, the halogenated compound may be formed by the replacement of a hydrogen atom by the halogenating species, as discussed above. Alternatively, the halogenated compound may be formed by the addition of the halogenating species to both carbon atoms of a carbon-carbon double bond, as also explained above. Alternatively, the halogenated compound may be formed by the replacement of a halogen atom by the halogenating species, as also discussed above. Finally, alternatively, the material to be halogenated and the halogenated compound may be inorganic, as discussed above.

Additional advantages and modifications will readily occur to those skilled in the art. The invention, in its broader aspects, is therefore not limited to the specific details and representative apparatus shown and described. Accordingly, departures may be made from such details without departing from the spirit or scope of the general inventive concept as defined by the appended claims and their equivalents.

**WHAT IS CLAIMED IS**

1. An electrochemical cell for producing in-situ a halogenated compound, comprising:
  - (a) inlet means for introducing anhydrous  
5 hydrogen halide and for co-feeding a material to be halogenated to an electrochemical cell;
  - (b) oxidizing means for oxidizing hydrogen halide to produce protons and a halogenating species, wherein the co-fed material reacts with the  
10 halogenating species to produce a halogenated compound;
  - (c) cation-transporting means for transporting the protons therethrough; and
  - (d) reducing means for reducing the protons  
15 to produce hydrogen.
2. The electrochemical cell of Claim 1, wherein the oxidizing means is an anode, the cation-transporting means is a membrane and the reducing means is a cathode.
- 20 3. The electrochemical cell of Claim 2, further including anode-side outlet means for releasing the halogenated compound and any unreacted hydrogen halide and co-fed material from the cell.
4. The electrochemical cell of Claim 2, further  
25 including cathode-side inlet means for delivering water to the membrane.
5. The electrochemical cell of Claim 5, further including a mass flow field disposed in contact with the anode and a cathode mass flow field disposed in  
30 contact with the cathode, wherein the anode mass flow field and the cathode mass flow field each have channels formed therein, and wherein the channels of the anode mass flow field and the channels of the cathode mass flow field are parallel to each other.
- 35 6. The electrochemical cell of Claim 5, wherein the channels of both the anode mass flow field and of the cathode mass flow field are vertical.

7. A process for the in-situ production of a halogenated compound, comprising the steps of:

- (a) supplying anhydrous hydrogen halide to an anode-side inlet of an electrochemical cell, where  
5 the cell comprises an anode disposed in contact with one side of a cation-transporting membrane and a cathode disposed in contact with another side of the membrane;
- (b) co-feeding a material to be halogenated  
10 to the inlet of the cell; and
- (c) applying a voltage to the electrochemical cell so that the anode is at a higher potential than the cathode and so that:
  - (i) the hydrogen halide is oxidized  
15 at the anode to produce protons and a halogenating species,
  - (ii) the co-fed material reacts with the halogenating species to produce a halogenated compound,
  - (iii) the halogenated compound is  
20 released from an anode-side outlet of the electrochemical cell,
  - (iv) the protons are transported through the membrane of the cell, and
  - (v) the protons are reduced at the  
25 cathode.

8. The process of Claim 7, wherein the halogenated compound is formed by the replacement of a hydrogen atom by the halogenating species.

30 9. The process of Claim 7, wherein the halogenated compound is formed by the addition of the halogenating species to both carbon atoms of a carbon-carbon double bond.

10. The process of Claim 7, wherein the  
35 halogenated compound is formed by the replacement of a halogen atom by the halogenating species.

11. The process of Claim 7, wherein the material to be halogenated and the halogenated compound are inorganic.

12. The process of Claim 7, wherein a portion of the hydrogen halide and a portion of the co-fed material are unreacted, and the unreacted hydrogen halide and the co-fed material are released from the anode-side outlet.

13. The process of Claim 7, wherein water is delivered to a cathode-side inlet of the cell.

14. The process of Claim 13, wherein the protons are reduced at the cathode to produce hydrogen.

15. The process of Claim 14, wherein the hydrogen and a portion of the water delivered to the cathode-side inlet are released through a cathode-side outlet of the cell.

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FIG. 1

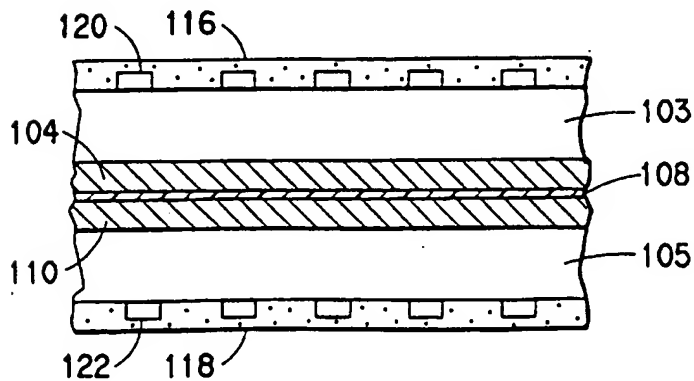
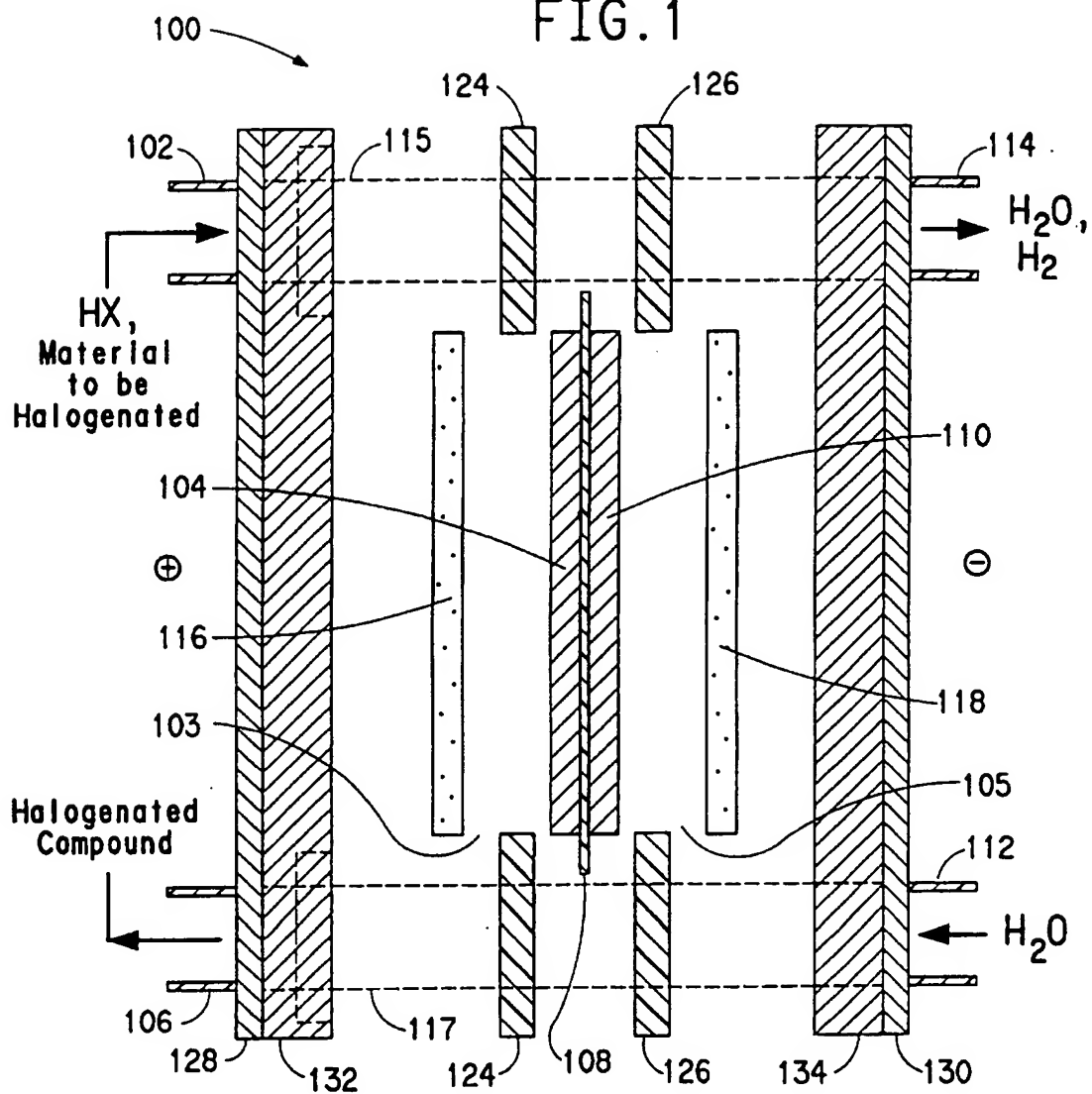


FIG. 1A

# INTERNATIONAL SEARCH REPORT

Intern. Appl. No.

PCT/US 97/10466

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C25B9/00 C25B3/06 C25B1/24

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C25B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 14797 A (E.I. DU PONT DE NEMOURS AND COMPANY) 1 June 1995 see page 12, line 18 - page 13, line 1 see page 14, line 25 - page 15, line 20 see figure 1	1-5
X	US 4 472 251 A (S.R. PICKENS) 18 September 1984 see column 4, line 15 - line 24	7, 10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Appl. Application No

PCT/US 97/10466

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